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VERIFICATION OF A TRANSLATION

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Director to RWS Group plc, of Europa House, Marham Way, Gerrards Cross, Buckinghamshire, England declare:

That the translator responsible for the attached translation is knowledgeable in the German language in which the below identified international application was filed, and that, to the best of RWS Group plc knowledge and belief, the English translation of the international application No. PCT/EP00/05825 is a true and complete translation of the above identified international application as filed.

I hereby declare that all the statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application issued thereon.

Date: November 27, 2001

Signature of Director :



For and on behalf of RWS Group plc

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June 15, 2000

Multicoat color and/or effect coating system, process  
for producing it and its use

The present invention relates to a novel multicoat  
5 color and/or effect coating system for a primed or an  
unprimed substrate. The present invention further  
relates to a novel process for producing a multicoat  
color and/or effect coating system on a primed or  
unprimed substrate. The present invention relates not  
10 least to the use of the novel multicoat and/or effect  
coating system, and of the novel process for producing  
it, in automotive OEM finishing and refinishing, in  
industrial coating, including container coating and  
coil coating, and in furniture coating.

15

Multicoat color and/or effect coating systems for  
primed or unprimed substrates are known. Normally, they  
comprise a surfacer coat, which absorbs mechanical  
energy, and a solid-color and/or effect topcoat. In  
20 another variant, they comprise a surfacer coat, a color  
and/or effect basecoat, and a clearcoat. For the  
coating of plastics, it is also common to employ a  
multicoat system which comprises a color and/or effect  
basecoat and a clearcoat. In many cases, such multicoat  
25 systems are produced by the wet-on-wet technique, in  
which in particular the basecoat film is merely dried

but not cured before the application of the clearcoat film, and the basecoat film and clearcoat film are cured together.

5 In the coating materials used to produce known multicoat color and/or effect coating systems, constituents are frequently used that are prepared by free-radical polymerization of olefinically unsaturated monomers. These constituents are also referred to as  
10 binders. In the majority of cases, the binders of said type comprise acrylate copolymers.

Acrylate copolymers and coating materials comprising them are described, for example, in the patents  
15 EP-B-0 447 428, EP-B-0 593 454, EP-B-0 052 776, or DE-A-42 04 518.

Acrylate copolymers may be prepared by well-known polymerization processes in bulk, solution or emulsion.  
20 Polymerization techniques for preparing acrylate copolymers, especially polyacrylate resins, are general knowledge and are widely described (cf., e.g., Houben-Weyl, Methoden der organischen Chemie, 4th Edition, Volume 14/1, pages 24 to 255 (1961)).

25

Further examples of suitable copolymerization processes for preparing acrylate copolymers are described in patents DE-A-197 09 465, DE-C-197 09 476,

DE-A-28 48 906, DE-A-195 24 182, EP-A-0 554 783,  
EP-B-0 650 979, WO 95/27742, DE-A-38 41 540, and  
WO 82/02387.

- 5 Suitable reactors for the copolymerization processes  
are the customary and known stirred vessels, cascades  
of stirred vessels, tube reactors, loop reactors, and  
Taylor reactors, as described for example in patents  
DE-B-1 071 241 and EP-A-0 498 583 or in the article by  
10 K. Kataoka in Chemical Engineering Science, Volume 50,  
No. 9, 1995, pages 1409 to 1416.

The free-radical polymerization used to prepare the  
acrylate copolymers is often very exothermic and  
15 difficult to control. The implications of this fact for  
the reaction regime are that it is necessary to avoid  
high monomer concentrations and/or the batch mode,  
where the entirety of the monomers is introduced as an  
initial charge in an aqueous medium, emulsified and  
20 subsequently polymerized to completion. Even the  
tailoring of defined molecular weights, molecular  
weight distributions, and other properties frequently  
causes difficulties. The tailoring of a certain profile  
of properties in the acrylate copolymers, however, is  
25 of great importance for their use as binders in coating  
materials, since by this means it is possible to  
influence the profile of performance properties of the  
coating materials in a direct way.

There has therefore been no lack of attempts to control the free-radical copolymerization of olefinically unsaturated monomers in a targeted manner.

5

For instance, International Patent Application WO 98/01478 describes a process in which the copolymerization is conducted in the presence of a free-radical initiator and of a thiocarbonylthio  
10 compound as chain transfer agent.

International Patent Application WO 92/13903 describes a process for preparing copolymers having a low molecular weight by means of free-radical chain  
15 polymerization in the presence of a group transfer agent containing a carbon-sulfur double bond. These compounds act not only as chain transfer agents but also as growth regulators, so that only low molecular weight copolymers result.

20

International Patent Application WO 96/15157 discloses a process for preparing copolymers having a comparatively narrow molecular weight distribution, in which a monomer is reacted with a vinyl-terminated  
25 macromonomer in the presence of a free-radical initiator.

Furthermore, International Patent Application WO 98/37104 discloses the preparation of acrylate copolymers having defined molecular weights by means of free-radical polymerization in the presence of a chain transfer agent containing a C-C double bond and containing radicals which activate this double bond in terms of the free-radical addition reaction of monomers.

10 Despite the significant progress in this area, there is still a lack of a universally applicable process of controlled free-radical polymerization which in a simple manner provides chemically structured polymers, especially acrylate copolymers, and by means of which  
15 it is possible to tailor the profile of properties of the polymers in respect of their use in coating materials, which are used to produce multicoat color and/or effect coating systems.

20 As a result, it continues to be necessary to take other measures, in some cases more complex ones, to harmonize the profiles of properties and material compositions of the surfacers, basecoat materials and clearcoat materials in such a way that the multicoat color and/or  
25 effect coating systems have the high optical quality and intercoat adhesion required by the market and no longer give rise to problems such as deficient condensation resistance of the surfacer coats, cracking

(mud cracking) in the basecoats, or leveling defects or surface structures in the clearcoats.

It is an object of the present invention to provide new  
5 multicoat color and/or effect coating systems and also  
new processes for producing them, in which at least one  
coat of the multicoat color and/or effect coating  
system is produced from a coating material which may be  
adapted in a simple manner to its respective use as  
10 surfacer, basecoat and/or clearcoat material. The aim  
is to realize this object in a simple manner by  
tailoring the profile of properties of the coating  
materials, in particular through the use of chemically  
structured polymers obtainable by means of controlled  
15 free-radical polymerization. The new multicoat color  
and/or effect coating systems which result should no  
longer have the disadvantages of the prior art but  
instead should exhibit outstanding optical quality,  
intercoat adhesion and condensation resistance and  
20 should not exhibit any cracking (mud cracking),  
leveling defects or surface structures. Moreover, it  
should be possible to use these chemically structured  
polymers as grinding resins which make it possible in  
an advantageous manner to provide pigment pastes having  
25 a particularly good capacity for incorporation by  
mixing for the surfacers, basecoat and clearcoat  
materials used to produce the new multicoat color  
and/or effect coating systems.

Accordingly, we have found the novel multicoat color  
and/or effect coating system ML for a primed or  
unprimed substrate, which comprises, lying above one  
5 another in the stated sequence

(1) a surfacer coat FL which absorbs mechanical  
energy, and

10 (2) a color and/or effect topcoat DL

or

(1) a surfacer coat FL which absorbs mechanical  
15 energy,

(2) a color and/or effect basecoat BL, and

(3) a clearcoat KL

20

or

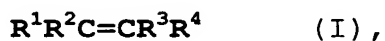
(1) a color and/or effect basecoat BL and

25 (2) a clearcoat KL,

wherein at least one coat FL and/or DL or BL and/or KL  
or FL, BL and/or KL, preferably at least two coats FL,

BL and/or KL or all coats FL and DL or BL and KL or FL,  
BL and KL of the multicoat system ML has or have been  
produced from a coating material comprising at least  
one constituent (A) preparable by free-radical  
5 polymerization of

- a) at least one olefinically unsaturated monomer,
- b) at least one olefinically unsaturated monomer  
10 different than the olefinically unsaturated  
monomer (a) and of the general formula I



15 in which the radicals  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  each  
independently of one another are hydrogen atoms or  
substituted or unsubstituted alkyl, cycloalkyl,  
alkylcycloalkyl, cycloalkylalkyl, aryl, alkylaryl,  
cycloalkylaryl, arylalkyl or arylcycloalkyl  
20 radicals, with the proviso that at least two of  
the variables  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are substituted or  
unsubstituted aryl, arylalkyl or arylcycloalkyl  
radicals, especially substituted or unsubstituted  
aryl radicals;

25

in an aqueous medium.

In the text below, the novel multicoat color and/or effect coating system ML for a primed or unprimed substrate is referred to as the "multicoat system ML of the invention".

5

We have also found the novel process for producing a multicoat color and/or effect coating system ML on a primed or unprimed substrate by

10 (I) preparing a surfacer film by applying a surfacer to the substrate,

(II) curing the surfacer film to give the surfacer coat FL,

15

(III) preparing a solid-color topcoat film by applying a solid-color coat material to the surfacer coat FL, and

20 (IV) curing the solid-color topcoat film to give the solid-color topcoat DL,

or

25 (I) preparing a basecoat film by applying a basecoat material to the substrate,

(II) drying the basecoat film,

(III) preparing a clearcoat film by applying a clearcoat material to the basecoat film, and

5 (IV) jointly curing the basecoat film and the clearcoat film to give the basecoat BL and the clearcoat KL,

or

10

(I) preparing a surfacer film by applying a surfacer to the substrate,

15

(II) curing the surfacer film to give the surfacer coat FL,

(III) preparing a basecoat film by applying a basecoat material to the surfacer coat FL,

20 (IV) drying the basecoat film,

(V) preparing a clearcoat film by applying a clearcoat material to the basecoat film, and

25 (VI) jointly curing the basecoat film and the clearcoat film to give the basecoat BL and the clearcoat KL,

in which at least one of the coating materials employed in each case comprises at least one constituent (A) preparable by free-radical polymerization of

- 5 a) at least one olefinically unsaturated monomer and
- b) at least one olefinically unsaturated monomer different than the olefinically unsaturated monomer (a) and of the general formula I

10



in which the radicals  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  each independently of one another are hydrogen atoms or substituted or unsubstituted alkyl, cycloalkyl, alkylcycloalkyl, cycloalkylalkyl, aryl, alkylaryl, cycloalkylaryl, arylalkyl or arylcycloalkyl radicals, with the proviso that at least two of the variables  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are substituted or unsubstituted aryl, arylalkyl or arylcycloalkyl radicals, especially substituted or unsubstituted aryl radicals;

in an aqueous medium.

25

In the text below, the novel process for producing a multicoat color and/or effect coating system ML on a

primed or unprimed substrate is referred to as the "process of the invention".

In the light of the prior art it was surprising that  
5 the complex object on which the present invention was  
based could be achieved by means of the process of the  
invention and the multicoat systems ML of the  
invention. A particular surprise was that the multicoat  
coating systems ML of the invention have outstanding  
10 optical quality, possess good intercoat adhesion and  
condensation resistance, and no longer exhibit cracking  
(mud cracking), leveling defects or surface structures.  
More surprising still was that the use of thixotropic  
agents or rheological assistance in basecoat materials  
15 used to produce perlescent effects and/or dichroic  
effects is substantially or, in some cases, entirely  
unnecessary.

In accordance with the invention, at least one coat of  
20 the multicoat system ML of the invention is produced  
from a coating material which comprises a constituent  
(A). It is of advantage in accordance with the  
invention if at least two coats, in particular all  
coats, of the multicoat system ML of the invention are  
25 produced from such coating materials.

In accordance with the invention, the constituent (A)  
is prepared by controlled free-radical polymerization

of at least one olefinically unsaturated monomer (a)  
and at least one olefinically unsaturated monomer (b)  
which is different than the monomer (a).

5 Examples of suitable monomers (a) are

10 a1) essentially acid-group-free (meth)acrylic esters  
such as (meth)acrylic alkyl or cycloalkyl esters  
having up to 20 carbon atoms in the alkyl radical,  
especially methyl, ethyl, propyl, n-butyl, sec-  
butyl, tert-butyl, hexyl, ethylhexyl, stearyl and  
lauryl acrylate or methacrylate; cycloaliphatic  
(meth)acrylic esters, especially cyclohexyl,  
isobornyl, dicyclopentadienyl, octahydro-4,7-  
15 methano-1H-indenemethanol or tert-butylcyclohexyl  
(meth)acrylate; (meth)acrylic oxaalkyl esters or  
oxacycloalkyl esters such as ethyltriglycol  
(meth)acrylate and methoxyoligoglycol (meth)-  
acrylate having a molecular weight Mn of  
20 preferably 550, or other ethoxylated and/or  
propoxylated hydroxyl-free (meth)acrylic acid  
derivatives. These may contain minor amounts of  
(meth)acrylic alkyl or cycloalkyl esters of higher  
functionality, such as the di(meth)acrylates of  
25 ethylene glycol, propylene glycol, diethylene  
glycol, dipropylene glycol, butylene glycol,  
1,5-pentanediol, 1,6-hexanediol, octahydro-4,7-  
methano-1H-indenedimethanol or 1,2-, 1,3- or

1,4-cyclohexanediol; trimethylolpropane di- or tri(meth)acrylate; or pentaerythritol di-, tri- or tetra(meth)acrylate. For the purposes of the present invention, minor amounts of monomers of higher functionality in this case are to be understood as amounts which do not lead to crosslinking or gelling of the copolymers (A).

- a2) Monomers which carry per molecule at least one hydroxyl group, amino group, alkoxymethylamino group or imino group and are essentially free from acid groups, such as hydroxyalkyl esters of acrylic acid, methacrylic acid or another alpha,beta-olefinically unsaturated carboxylic acid, which derive from an alkylene glycol esterified with the acid, or which are obtainable by reacting the alpha,beta-olefinically unsaturated carboxylic acid with an alkylene oxide, especially hydroxyalkyl esters of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid or itaconic acid in which the hydroxyalkyl group contains up to 20 carbon atoms, such as 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 3-hydroxybutyl, 4-hydroxybutyl acrylate, methacrylate, ethacrylate, crotonate, maleate, fumarate or itaconate; or hydroxycycloalkyl esters such as 1,4-bis(hydroxymethyl)cyclohexane, octahydro-4,7-

methano-1H-indenedimethanol or methylpropanediol  
monoacrylate, monomethacrylate, monoethacrylate,  
monocrotonate, monomaleate, monofumarate or  
monoitaconate; or reaction products of cyclic  
5 esters, such as epsilon-caprolactone, for example,  
and these hydroxyalkyl or hydroxycycloalkyl  
esters; or olefinically unsaturated alcohols such  
as allyl alcohol or polyols such as  
trimethylolpropane monoallyl or diallyl ether or  
10 pentaerythritol monoallyl, diallyl or triallyl  
ether (as far as these monomers (a2) of higher  
functionality are concerned, the comments made  
above relating to the monomers (a1) of higher  
functionality apply analogously); N,N-dimethyl-  
15 aminoethyl acrylate, N,N-diethylaminoethyl  
methacrylate, allylamine or N-methyliminoethyl  
acrylate or N,N-di(methoxymethyl)aminoethyl  
acrylate and methacrylate or N,N-di(butoxymethyl)-  
aminopropyl acrylate and methacrylate; monomers of  
20 this kind are used preferably to prepare self-  
crosslinking constituents (A).

a3) Monomers which carry per molecule at least one  
acid group which can be converted into the  
25 corresponding acid anion group, such as acrylic  
acid, methacrylic acid, ethacrylic acid, crotonic  
acid, maleic acid, fumaric acid or itaconic acid;  
olefinically unsaturated sulfonic or phosphonic

acids or their partial esters; or mono(meth)-acryloyloxyethyl maleate, succinate or phthalate.

- a4) Vinyl esters of alpha-branched monocarboxylic acids having 5 to 18 carbon atoms in the molecule. The branched monocarboxylic acids can be obtained by reacting formic acid or carbon monoxide and water with olefins in the presence of a liquid, strongly acidic catalyst; the olefins may be cracking products of paraffinic hydrocarbons, such as mineral oil fractions, and may comprise both branched and straight-chain acyclic and/or cycloaliphatic olefins. The reaction of such olefins with formic acid or, respectively, with carbon monoxide and water produces a mixture of carboxylic acids in which the carboxyl groups are located predominantly on a quaternary carbon atom. Examples of other olefinic starting materials are propylene trimer, propylene tetramer and diisobutylene. Alternatively, the vinyl esters (a4) may be prepared in a conventional manner from the acids, by reacting, for example, the acid with acetylene. Particular preference, owing to their ready availability, is given to using vinyl esters of saturated aliphatic monocarboxylic acids having 9 to 11 carbon atoms that are branched on the alpha carbon atom, but especially Versatic® acids.

- a5) Reaction products of acrylic acid and/or methacrylic acid with the glycidyl ester of an alpha-branched monocarboxylic acid having 5 to 18 carbon atoms per molecule, especially a Versatic® acid, or, instead of the reaction product, an equivalent amount of acrylic acid and/or methacrylic acid which is then reacted during or after the polymerization reaction with the glycidyl ester of an alpha-branched monocarboxylic acid having 5 to 18 carbon atoms per molecule, especially a Versatic® acid.
- a6) Cyclic and/or acyclic olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, cyclohexene, cyclopentene, norbornene, butadiene, isoprene, cyclopentadiene and/or dicyclopentadiene.
- a7) (Meth)acrylamides such as (meth)acrylamide, N-methyl-, N,N-dimethyl-, N-ethyl-, N,N-diethyl-, N-propyl-, N,N-dipropyl-, N-butyl-, N,N-dibutyl-, N-cyclohexyl-, N,N-cyclohexylmethyl- and/or N-methylol-, N,N-dimethylol-, N-methoxymethyl-, N,N-di(methoxymethyl)-, N-ethoxymethyl- and/or N,N-di(ethoxyethyl)-(meth)acrylamide. Monomers of

the last-mentioned kind are used in particular to prepare self-crosslinking constituents (A).

- a8) Monomers containing epoxide groups, such as the glycidyl esters of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid and/or itaconic acid.
- a9) Vinylaromatic hydrocarbons such as styrene, alpha-alkylstyrenes, especially alpha-methylstyrene, and/or vinyltoluene; vinylbenzoic acid (all isomers), N,N-diethylaminostyrene (all isomers), alpha-methylvinylbenzoic acid (all isomers), N,N-diethylamino-alpha-methylstyrene (all isomers) and/or p-vinylbenzenesulfonic acid.
- a10) Nitriles such as acrylonitrile and/or methacrylonitrile.
- a11) Vinyl compounds, especially vinyl halides and/or vinylidene dihalides such as vinyl chloride, vinyl fluoride, vinylidene dichloride or vinylidene difluoride; N-vinylamides such as vinyl-N-methylformamide, N-vinylcaprolactam, 1-vinylimidazole or N-vinylpyrrolidone; vinyl ethers such as ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether and/or vinyl cyclohexyl

ether; and/or vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pivalate and/or the vinyl ester of 2-methyl-2-ethyl-heptanoic acid.

5

a12) Allyl compounds, especially allyl ethers and allyl esters such as allyl methyl, ethyl, propyl or butyl ether or allyl acetate, propionate or butyrate.

10

a13) Polysiloxane macromonomers having a number-average molecular weight  $M_n$  of from 1000 to 40 000 and having on average from 0.5 to 2.5 ethylenically unsaturated double bonds per molecule; especially

15

polysiloxane macromonomers having a number-average molecular weight  $M_n$  of from 2000 to 20 000, with particular preference from 2500 to 10 000 and, in particular, from 3000 to 7000 and having on average from 0.5 to 2.5, preferably from 0.5 to

20

1.5, ethylenically unsaturated double bonds per molecule, as are described in DE-A 38 07 571 A1 on pages 5 to 7, in DE-A 37 06 095 in columns 3 to 7, in EP-B 0 358 153 on pages 3 to 6, in US-A 4,754,014 in columns 5 to 9, in DE-A 44 21 823 or in International Patent Application WO 92/22615 on page 12 line 18 to page 18 line 10.

25

and/or

a14) Acryloxysilane-containing vinyl monomers,  
preparable by reacting hydroxyl-functional silanes  
5 with epichlorohydrin and then reacting the  
reaction product with (meth)acrylic acid and/or  
with hydroxyalkyl and/or hydroxycycloalkyl esters  
of (meth)acrylic acid (cf. monomers a2).

10 Each of the abovementioned monomers (a1) to (a14) may  
be polymerized on their own with the monomers (b). In  
accordance with the invention, however, it is  
advantageous to use at least two monomers (a), since by  
this means it is possible to vary the profile of  
15 properties of the resulting constituents (A), i.e.,  
copolymers (A), very widely, in a particularly  
advantageous manner, and to tailor said profile of  
properties specifically to the particular intended use  
of the coating material. In particular, it is possible  
20 in this way to incorporate into the copolymers (A)  
functional groups by means of which the copolymers (A)  
become hydrophilic, so that they may be dissolved or  
dispersed in aqueous media. It is also possible to  
incorporate functional groups (afg) capable of entering  
25 into thermal crosslinking reactions with the  
complementary functional groups (bfg), described below,  
of the crosslinking agents (B). It is also possible to  
incorporate functional groups which give the

constituent(A) self-crosslinking properties, such as N-methylol groups or N-alkoxymethyl groups.

In accordance with the invention, very particular  
5 advantages result if the monomers (a) used comprise the monomers (a1) and (a2) and also, if desired, (a3).

In accordance with the invention, the monomers (b) used comprise compounds of the general formula I.

10

In the general formula I, the radicals  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  each independently of one another are hydrogen atoms or substituted or unsubstituted alkyl, cycloalkyl, alkylcycloalkyl, cycloalkylalkyl, aryl, alkylaryl, cycloalkylaryl, arylalkyl or arylcycloalkyl radicals,  
15 with the proviso that at least two of the variables  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are substituted or unsubstituted aryl, arylalkyl or arylcycloalkyl radicals, especially substituted or unsubstituted aryl radicals.

20

Examples of suitable alkyl radicals are methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, amyl, hexyl or 2-ethylhexyl.

25 Examples of suitable cycloalkyl radicals are cyclobutyl, cyclopentyl or cyclohexyl.

Examples of suitable alkylcycloalkyl radicals are methylenecyclohexane, ethylenecyclohexane or propane-1,3-diylcyclohexane.

- 5 Examples of suitable cycloalkylalkyl radicals are 2-, 3- or 4-methyl-, -ethyl-, -propyl- or -butylcyclohex-1-yl.

10 Examples of suitable aryl radicals are phenyl, naphthyl or biphenyl, preferably phenyl and naphthyl, and especially phenyl.

15 Examples of suitable alkylaryl radicals are benzyl or ethylene- or propane-1,3-diylbenzene.

Examples of suitable cycloalkylaryl radicals are 2-, 3- or 4-phenylcyclohex-1-yl.

20 Examples of suitable arylalkyl radicals are 2-, 3- or 4-methyl-, -ethyl-, -propyl- or -butylphen-1-yl.

Examples of suitable arylcycloalkyl radicals are 2-, 3- or 4-cyclohexylphen-1-yl.

25 The above-described radicals  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  may be substituted. The substituents used may comprise electron-withdrawing or electron-donating atoms or organic radicals.

Examples of suitable substituents are halogen atoms, especially chlorine and fluorine, nitrile groups, nitro groups, partially or fully halogenated, especially  
5 chlorinated and/or fluorinated, alkyl, cycloalkyl, alkylcycloalkyl, cycloalkylalkyl, aryl, alkylaryl, cycloalkylaryl, arylalkyl and arylcycloalkyl radicals, including those exemplified above, especially tert-butyl; aryloxy, alkyloxy and cycloalkyloxy radicals,  
10 especially phenoxy, naphthoxy, methoxy, ethoxy, propoxy, butyloxy or cyclohexyloxy; arylthio, alkylthio and cycloalkylthio radicals, especially phenylthio, naphthylthio, methylthio, ethylthio, propylthio, butylthio or cyclohexylthio; hydroxyl groups; and/or  
15 primary, secondary and/or tertiary amino groups, especially amino, N-methylamino, N-ethylamino, N-propylamino, N-phenylamino, N-cyclohexylamino, N,N-dimethylamino, N,N-diethylamino, N,N-dipropylamino, N,N-diphenylamino, N,N,-dicyclohexylamino, N-cyclo-  
20 hexyl-N-methylamino and N-ethyl-N-methylamino.

Examples of monomers (b) whose use is particularly preferred in accordance with the invention are diphenylethylene, dinaphthaleneethylene, cis- or  
25 trans-stilbene, vinylidenebis(4-N,N-dimethylamino-benzene), vinylidenebis(4-aminobenzene), and vinylidenebis(4-nitrobenzene).

In accordance with the invention, the monomers (b) may be used individually or as a mixture of at least two monomers (b).

5 In terms of the reaction regime and the properties of the resultant copolymers (A), especially the acrylate copolymers (A), diphenylethylene is of very particular advantage and is therefore used with very particular preference in accordance with the invention.

10

The monomers (a) and (b) to be used in accordance with the invention are reacted with one another in the presence of at least one free-radical initiator to form the copolymer (A). Examples of initiators which can be  
15 used are: dialkyl peroxides, such as di-tert-butyl peroxide or dicumyl peroxide; hydroperoxides, such as cumene hydroperoxide or tert-butyl hydroperoxide; peresters, such as tert-butyl perbenzoate, tert-butyl perpivalate, tert-butyl per-3,5,5-trimethylhexanoate or  
20 tert-butyl per-2-ethylhexanoate; potassium, sodium or ammonium peroxodisulfate; azodinitriles such as azobisisobutyronitrile; C-C-cleaving initiators such as benzpinacol silyl ethers; or a combination of a nonoxidizing initiator with hydrogen peroxide.

25

It is preferred to add comparatively large amounts of free-radical initiator, the proportion of the initiator in the reaction mixture being, based in each case on

the overall amount of the monomers (a) and of the initiator, with particular preference from 0.5 to 50% by weight, with very particular preference from 1 to 20% by weight, and in particular from 2 to 15% by weight.

Preferably, the weight ratio of initiator to the monomers (b) is from 4:1 to 1:4, with particular preference from 3:1 to 1:3, and in particular from 2:1 to 1:2. Further advantages result if the initiator is used in excess within the stated limits.

The free-radical copolymerization is preferably conducted in the apparatus mentioned at the outset, especially stirred vessels or Taylor reactors, the Taylor reactors being designed such that the conditions of Taylor flow are met over the entire reactor length, even if the kinematic viscosity of the reaction medium alters greatly, and in particular increases, owing to the copolymerization.

In accordance with the invention, the copolymerization is conducted in an aqueous medium.

The aqueous medium comprises essentially water. The aqueous medium may here include minor amounts of the below-detailed crosslinking agents (B), reactive diluents (F), coatings additives (G) and/or organic

solvents (H) and/or other dissolved solid, liquid or gaseous organic and/or inorganic substances of low and/or high molecular mass, especially surface-active substances, provided these do not adversely affect, or  
5 even inhibit, the copolymerization. In the context of the present invention, a "minor amount" is to be understood as an amount which does not remove the aqueous character of the aqueous medium.

10 Alternatively, the aqueous medium may comprise straight water.

The copolymerization is preferably conducted in the presence of at least one base. Particular preference is  
15 given to low molecular mass bases such as sodium hydroxide solution, potassium hydroxide solution, ammonia, diethanolamine, triethanolamine, mono-, di- and triethylamine, and/or dimethylethanolamine, especially ammonia and/or di- and/or triethanolamine.

20

The copolymerization is advantageously conducted at temperatures above room temperature and below the lowest decomposition temperature of the monomers used in each case, preference being given to a chosen  
25 temperature range of from 10 to 150°C, with very particular preference from 70 to 120°C, and in particular from 80 to 110°C.

When using particularly volatile monomers (a) and/or (b), the copolymerization may also be conducted under pressure, preferably under from 1.5 to 3000 bar, with particular preference from 5 to 1500 bar, and in particular from 10 to 1000 bar.

In terms of the molecular weight distribution, there are no restrictions whatsoever imposed on the constituent (A). Advantageously, however, the copolymerization is conducted so as to give a molecular weight distribution  $M_w/M_n$ , measured by gel permeation chromatography using polystyrene as standard, of  $\leq 4$ , with particular preference  $\leq 2$ , and in particular  $\leq 1.5$ , and in certain cases even  $\leq 1.3$ . The molecular weights of the constituents (A) may be controlled within wide limits by the choice of ratio of monomer (a) to monomer (b) to free-radical initiator. In this context, the amount of monomer (b) in particular determines the molecular weight, specifically such that, the higher the proportion of monomer (b), the lower the resultant molecular weight.

The constituent (A) resulting from the copolymerization is obtained as a mixture with the aqueous medium, generally in the form of a dispersion. In this form it can be processed further directly or else used as a macroinitiator for further reaction with at least one

further monomer (a) in a second stage (ii). The constituent (A) resulting in the first stage (i), however, may also be isolated as a solid and then reacted further.

5

The further reaction in accordance with the stage (ii) is preferably conducted under the standard conditions for a free-radical polymerization, it being possible for suitable solvents (H) and/or reactive diluents (F) to be present. Stages (i) and (ii) in the context of the process of the invention may be conducted separately from one another, both spatially and temporally. In addition, however, stages (i) and (ii) may also be carried out in succession in one reactor.

10 For this purpose, the monomer (b) is first reacted with at least one monomer (a), completely or partially depending on the desired application and the desired properties, after which at least one further monomer (a) is added and the mixture is subjected to free-

15 radical polymerization. In another embodiment, at least two monomers (a) are used from the start, the monomer (b) being first reacted with one of the at least two monomers (a) and then the resultant reaction product (A) being reacted, above a certain molecular weight,

20 with the further monomer (a) as well.

25

Depending on the reaction regime, it is possible in accordance with the invention to prepare endgroup-

functionalized polymers, block, multiblock and gradient copolymers, star polymers, graft copolymers, and branched copolymers as constituents (A).

- 5 The constituent (A) may include at least one, preferably at least two, functional groups (afg) which are able to enter into thermal crosslinking reactions with complementary functional groups (bfg) of the crosslinking agents (B) described below. The functional
- 10 groups (afg) may be introduced into the constituent (A) by way of the monomers (a) or may be introduced following its synthesis, by means of polymer-analogous reactions.
- 15 Examples of suitable complementary reactive functional groups (afg) and (bfg) which enter into crosslinking reactions, for use in accordance with the invention, are summarized in the following overview. In the overview, the variable  $R^5$  is substituted or
- 20 unsubstituted alkyl, cycloalkyl, alkylcycloalkyl, cycloalkylalkyl, aryl, alkylaryl, cycloalkylaryl, arylalkyl or arylcycloalkyl radicals; the variables  $R^6$  and  $R^7$  are identical or different alkyl, cycloalkyl, alkylcycloalkyl or cycloalkylalkyl radicals, or are
- 25 linked with one another to form an aliphatic or heteroaliphatic ring. Examples of suitable radicals of this kind are those listed above in connection with the radicals  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$ .

Overview: Examples of complementary functional groups  
(afg) and (bfg) in the

5 constituent (A) and crosslinking agent (B)

or

crosslinking agent (B) and constituent (A)

-SH

-C(O)-OH

-NH<sub>2</sub>

-C(O)-O-C(O)-

-OH

-NCO

-O-(CO)-NH-(CO)-NH<sub>2</sub>

-NH-C(O)-OR<sup>5</sup>

-O-(CO)-NH<sub>2</sub>

-CH<sub>2</sub>-OH

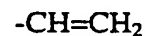
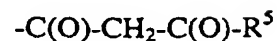
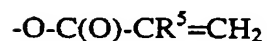
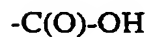
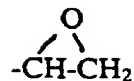
-CH<sub>2</sub>-O-CH<sub>3</sub>

-NH-C(O)-CH(-C(O)OR<sup>5</sup>)<sub>2</sub>

-NH-C(O)-CH(-C(O)OR<sup>5</sup>)(-C(O)-R<sup>5</sup>)

-NH-C(O)-NR<sup>6</sup>R<sup>7</sup>

= Si(OR<sup>5</sup>)<sub>2</sub>



The selection of the respective complementary groups (afg) and (bfg) is guided on the one hand by the consideration that, during storage, they should not enter into any unwanted reactions and/or should not disrupt or inhibit curing, if appropriate, with actinic radiation, and on the other hand by the temperature range within which thermal curing is to take place.

10 In this context, especially with regard to heat-sensitive substrates such as plastics, it is of advantage in accordance with the invention to choose a temperature range which does not exceed 100°C, and in particular does not exceed 80°C. In the light of these  
15 boundary conditions, complementary functional groups which have proven advantageous are hydroxyl groups and

isocyanate groups, or carboxyl groups and epoxy groups, which are therefore employed with preference, in accordance with the invention, in the coating materials of the invention that are present as two-component or  
5 multi-component systems. Particular advantages result if the hydroxyl groups are used as functional groups (afg) and the isocyanate groups as functional groups (bfg).

10 If higher crosslinking temperatures, for example from 100°C to 180°C, may be employed, which is preferred in accordance with the invention, suitable coating materials also include one-component systems, in which the functional groups (afg) are preferably thio, amino,  
15 hydroxyl, carbamate, allophanate, carboxyl and/or (meth)acrylate groups, but especially hydroxyl groups, and the functional groups (bfg) are preferably anhydride, carboxyl, epoxy, blocked isocyanate, urethane, methylol, methylol ether, siloxane, amino,  
20 hydroxyl and/or beta-hydroxyalkylamide groups.

The constituent (A) and, respectively, the coating material produced using it, however, may also film without a crosslinking agent (B) and still form an  
25 ideal coating. In this case, the constituent (A) is physically curing. In the context of the present invention, physical curing and curing by way of the

above-described complementary groups (afg) and (bfg) are collected together under the term "thermal curing".

The proportion of the constituent (A) for use in accordance with the invention in the coating material may vary very widely and is also guided in particular by whether the coating material is to be used for the mechanical-energy-absorbing surfacer coat FL, the color and/or effect topcoat DL, the color and/or effect basecoat BL, or the clearcoats KL. Advantageously, the proportion is from 1 to 90, preferably from 2 to 80, with particular preference from 3 to 75, and in particular from 4 to 70% by weight, based in each case on the overall solids content of the coating material.

15

The coating material may further comprise at least one constituent (A') comprising a customary and known binder (A') with at least one functional group (afg). Examples of suitable binders (A') are linear and/or branched and/or block, comb and/or random poly(meth)acrylates or acrylate copolymers, polyesters, alkyds, amino resins, polyurethanes, acrylated polyurethanes, acrylated polyesters, polylactones, polycarbonates, polyethers, epoxy resin-amine adducts, (meth)acrylate diols, partially hydrolyzed polyvinyl esters or polyureas, which contain said functional groups (afg). If used, their proportion in the coating material of the invention is preferably from 1 to 50,

preferably from 2 to 40, with particular preference from 3 to 30, and in particular from 4 to 25% by weight, based in each case on the overall solids content of the coating material.

5

The coating material may further comprise at least one crosslinking agent (B) which contains at least two, especially three, of the complementary functional groups (bfg) described in detail above.

10

Where the coating material comprises a two-component or multicomponent system, polyisocyanates and/or polyepoxides, but especially polyisocyanates, are used as crosslinking agents (B).

15

Examples of suitable polyisocyanates (B) are organic polyisocyanates, especially so-called paint polyisocyanates, having free isocyanate groups attached to aliphatic, cycloaliphatic, araliphatic and/or aromatic  
20 moieties. Preference is given to polyisocyanates having from 2 to 5 isocyanate groups per molecule and viscosities of from 100 to 10 000, preferably from 100 to 5000, and in particular from 100 to 2000 mPa.s (at 23°C). If desired, small amounts of organic solvent  
25 (H), preferably from 1 to 25% by weight based on straight polyisocyanate, may be added to the polyisocyanates in order to make it easier to incorporate the isocyanate and, if appropriate, to

reduce the viscosity of the polyisocyanate to a level within the abovementioned ranges. Examples of suitable solvent additives to the polyisocyanates are ethoxyethyl propionate, amyl methyl ketone, and butyl acetate. Furthermore, the polyisocyanates (B) may have been hydrophilically or hydrophobically modified in a customary and known manner.

Examples of suitable polyisocyanates (B) are described, for example, in "Methoden der organischen Chemie", Houben-Weyl, Volume 14/2, 4th Edition, Georg Thieme Verlag, Stuttgart, 1963, pages 61 to 70, and by W. Siefken, Liebigs Annalen der Chemie, Volume 562, pages 75 to 136.

15

Further examples of suitable polyisocyanates (B) are polyisocyanates containing isocyanurate, biuret, allophanate, iminooxadiazinedione, urethane, urea and/or uretdione groups. Polyisocyanates containing urethane groups, for example, are prepared by reacting some of the isocyanate groups with polyols, such as trimethylolpropane and glycerol, for example. Preference is given to the use of aliphatic or cycloaliphatic polyisocyanates, especially hexamethylene diisocyanate, dimerized and trimerized hexamethylene diisocyanate, isophorone diisocyanate, 2-isocyanatopropylcyclohexyl isocyanate, dicyclohexylmethane 2,4'-diisocyanate, dicyclohexylmethane 4,4'-

diisocyanate, or 1,3-bis(isocyanatomethyl)cyclohexane (BIC), diisocyanates derived from dimeric fatty acids, as marketed under the commercial designation DDI.1410 by Henkel, 1,8-diisocyanato-4-isocyanatomethyloctane, 5 1,7-diisocyanato-4-isocyanatomethylheptane or 1-isocyanato-2-(3-isocyanatopropyl)cyclohexane, or mixtures of these polyisocyanates.

Examples of suitable polyepoxides (B) are all known 10 aliphatic and/or cycloaliphatic and/or aromatic polyepoxides, examples being those based on bisphenol A or bisphenol F. Other suitable examples of polyepoxides are the polyepoxides available commercially under the designations Epikote® from Shell, Denacol® from Nagase 15 Chemicals Ltd., Japan, such as Denacol EX-411 (pentaerythritol polyglycidyl ether), Denacol EX-321 (trimethylolpropane polyglycidyl ether), Denacol EX-512 (polyglycerol polyglycidyl ether), and Denacol EX-521 (polyglycerol polyglycidyl ether).

20

In the case of the one-component systems, the crosslinking agents (B) used react at relatively high temperatures with the functional groups of the binders to build up a three-dimensional network. Of course, 25 such crosslinking agents (B) may be used as well in the multicomponent systems, in minor amounts. In the context of the present invention, a "minor amount" is a

proportion which does not disrupt, let alone prevent, the principal crosslinking reaction.

5 Examples of suitable crosslinking agents (B) of this kind are blocked polyisocyanates. Examples of suitable polyisocyanates for preparing the blocked polyisocyanates are those described above.

10 Examples of suitable blocking agents are the blocking agents known from U.S. Patent US-A-4,444,954, such as

i) phenols such as phenol, cresol, xylenol, nitrophenol, chlorophenol, ethylphenol, t-butylphenol, hydroxybenzoic acid, esters of this acid,  
15 or 2,5-di-tert-butyl-4-hydroxytoluene;

ii) lactams, such as  $\epsilon$ -caprolactam,  $\delta$ -valerolactam,  $\gamma$ -butyrolactam or  $\beta$ -propiolactam;

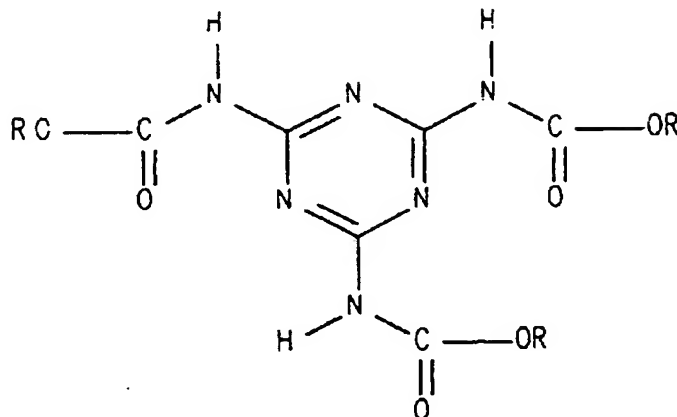
20 iii) active methylenic compounds, such as diethyl malonate, dimethyl malonate, ethyl or methyl acetoacetate, or acetylacetone;

iv) alcohols such as methanol, ethanol, n-propanol,  
25 isopropanol, n-butanol, isobutanol, t-butanol, n-amyl alcohol, t-amyl alcohol, lauryl alcohol, ethylene glycol monomethyl ether, ethylene glycol

- monoethyl ether, ethylene glycol monobutyl ether,  
diethylene glycol monomethyl ether, diethylene  
glycol monoethyl ether, propylene glycol  
monomethyl ether, methoxymethanol, glycolic acid,  
5 glycolic esters, lactic acid, lactic esters,  
methylolurea, methylolmelamine, diacetone alcohol,  
ethylenechlorohydrin, ethylenebromohydrin, 1,3-  
dichloro-2-propanol, 1,4-cyclohexyldimethanol or  
acetocyanohydrin;
- 10
- v) mercaptans such as butyl mercaptan, hexyl  
mercaptan, t-butyl mercaptan, t-dodecyl mercaptan,  
2-mercaptobenzothiazole, thiophenol, methylthio-  
phenol or ethylthiophenol;
- 15
- vi) acid amides such as acetoanilide, acetoanisidin-  
amide, acrylamide, methacrylamide, acetamide,  
stearamide or benzamide;
- 20 vii) imides such as succinimide, phthalimide or  
maleimide;
- viii) amines such as diphenylamine, phenylnaphthylamine,  
xylidine, N-phenylxylidine, carbazole, aniline,  
25 naphthylamine, butylamine, dibutylamine or butyl-  
phenylamine;
- ix) imidazoles such as imidazole or 2-ethylimidazole;

- x) ureas such as urea, thiourea, ethyleneurea, ethylenethiourea or 1,3-diphenylurea;
- 5 xi) carbamates such as phenyl N-phenylcarbamate or 2-oxazolidone;
- xii) imines such as ethyleneimine;
- 10 xiii) oximes such as acetone oxime, formaldoxime, acetaldoxime, acetoxime, methyl ethyl ketoxime, diisobutyl ketoxime, diacetyl monoxime, benzophenone oxime or chlorohexanone oximes;
- 15 xiv) salts of sulfurous acid such as sodium bisulfite or potassium bisulfite;
- xv) hydroxamic esters such as benzyl methacrylohydroxamate (BMH) or allyl methacrylohydroxamate;
- 20 or
- xvi) substituted pyrazoles, imidazoles or triazoles; and also
- 25 mixtures of these blocking agents, especially dimethylpyrazole and triazoles, malonic esters and acetoacetic esters or dimethylpyrazole and succinimide.

As crosslinking agents (B) it is also possible to use tris(alkoxycarbonylamino)triazines (TACTs) of the general formula



5

Examples of suitable tris(alkoxycarbonylamino)triazines (B) are described in patents US-A-4,939,213, US-A-5,084,541, and EP-A-0 624 577. Use is made in particular of the tris(methoxy-, tris(butoxy- and/or tris(2-ethylhexoxycarbonylamino)triazines.

The methyl butyl mixed esters, the butyl 2-ethylhexyl mixed esters, and the butyl esters are of advantage. They have the advantage over the straight methyl ester of better solubility in polymer melts, and also have less of a tendency to crystallize out.

Especially suitable crosslinking agents (B) are amino resins, examples being melamine resins, guanamine resins, and urea resins. Any amino resin suitable for

transparent topcoats or clearcoats, or a mixture of such amino resins, may be used here. For further details, reference is made to Römpp Lexikon "Lacke und Druckfarben", Georg Thieme Verlag, 1998, page 29, 5 "Amino resins", and the textbook "Lackadditive" [Additives for Coatings] by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998, pages 242 ff., or the book "Paints, Coatings and Solvents", second, completely revised edition, D. Stoye and W. Freitag (eds.), Wiley- 10 VCH, Weinheim, New York, 1998, pages 80 ff. Also suitable are the customary and known amino resins some of whose methylo and/or methoxymethyl groups have been defunctionalized by means of carbamate or allophanate groups. Crosslinking agents of this kind are described 15 in patents US-A-4,710,542 and EP-B-0 245 700 and also in the article by B. Singh and coworkers, "Carbamylmethylated Melamines, Novel Crosslinkers for the Coatings Industry" in Advanced Organic Coatings Science and Technology Series, 1991, Volume 13, pages 20 193 to 207.

Further examples of suitable crosslinking agents (B) are beta-hydroxyalkylamides such as N,N,N',N'-tetra- kis(2-hydroxyethyl)adipamide or N,N,N',N'-tetrakis(2- 25 hydroxypropyl)adipamide.

Further examples of suitable crosslinking agents (B) are siloxanes, especially siloxanes containing at least one trialkoxysilane or dialkoxysilane group.

- 5 Further examples of suitable crosslinking agents (B) are polyanhydrides, especially polysuccinic anhydride.

Further examples of suitable crosslinking agents (B) are compounds containing on average at least two groups  
10 amenable to transesterification, examples being reaction products of malonic diesters and polyisocyanates or reaction products of monoisocyanates with esters and partial esters of malonic acid with polyhydric alcohols, as described in European Patent  
15 EP-A-0 596 460.

The amount of the crosslinking agents (B) in the coating material may vary widely and is guided in particular, firstly, by the functionality of the  
20 crosslinking agents (B) and, secondly, by the number of crosslinking functional groups (afg) which are present in the binder (A), and also by the target crosslinking density. The skilled worker is therefore able to determine the amount of the crosslinking agents (B) on  
25 the basis of his or her general knowledge in the art, possibly with the aid of simple rangefinding experiments. Advantageously, the crosslinking agent (B) is present in the coating material of the invention in

an amount of from 1 to 60, preferably from 2 to 50, and in particular from 3 to 45% by weight, based in each case on the overall solids content of the coating material of the invention. It is further advisable here  
5 to choose the amounts of crosslinking agent (B) and binder (A) such that in the coating material the ratio of functional groups (bfg) in the crosslinking agent (B) to functional groups (afg) in the binder (A) is from 2:1 to 1:2, preferably from 1.5:1 to 1:1.5, with  
10 particular preference from 1.2:1 to 1:1.2, and in particular from 1.1:1 to 1:1.1.

If the coating material is to be curable not only thermally but also with actinic radiation, especially  
15 UV radiation and/or electron beams (dual cure), it comprises at least one constituent (C) which is curable with actinic radiation. If, however, the coating material is to be curable predominantly (dual cure) or exclusively with actinic radiation, a circumstance  
20 which in the context of the process of the invention is particularly relevant to clearcoat materials, it must comprise a constituent (C).

Suitable constituents (C) are in principle all  
25 oligomeric and polymeric compounds that are curable with actinic radiation, especially UV radiation and/or electron beams, said compounds being commonly used in

the field of UV curable or electron beam curable coating materials.

Radiation curable binders are used advantageously as  
5 constituents (C). Examples of suitable radiation  
curable binders (C) are (meth)acrylic-functional  
(meth)acrylic copolymers, polyether acrylates,  
polyester acrylates, unsaturated polyesters, epoxy  
acrylates, urethane acrylates, amino acrylates,  
10 melamine acrylates, silicone acrylates, isocyanato  
acrylates, and the corresponding methacrylates. It is  
preferred to use binders (C) that are free from  
aromatic structural units. Preference is therefore  
given to the use of urethane (meth)acrylates and/or  
15 polyester (meth)acrylates, with particular preference  
going to aliphatic urethane acrylates.

Where constituents (C) are used, they are present in  
the coating material in an amount of preferably from  
20 1 to 80, more preferably from 1.5 to 70, with  
particular preference from 2 to 65, and in particular  
from 2.5 to 60% by weight, based in each case on the  
overall solids content of the coating material.

25 The coating material may further comprise at least one  
photoinitiator (D). If the coating material or the  
coats produced from it is/are to be crosslinked  
additionally (dual cure) or exclusively with UV

radiation in the context of the process of the invention, it is generally necessary to use a photoinitiator (D). Where used, it is present in the coating material of the invention in fractions of  
5 preferably from 0.01 to 10, more preferably from 0.1 to 8, and in particular from 0.5 to 6% by weight, based in each case on the overall solids content of the coating material of the invention.

10 Examples of suitable photoinitiators (D) are those of the Norrish II type, whose mechanism of action is based on an intramolecular variant of the hydrogen abstraction reactions as occur diversely in photochemical reactions (reference may be made here, by  
15 way of example, to Römpp Chemie Lexikon, 9th, expanded and revised edition, Georg Thieme Verlag, Stuttgart, Vol. 4, 1991) or cationic photoinitiators (reference may be made here, by way of example, to Römpp Lexikon "Lacke und Druckfarben", Georg Thieme Verlag,  
20 Stuttgart, 1998, pages 444 to 446), especially benzophenones, benzoin ethers, or phosphine oxides. It is also possible to use, for example, the products available commercially under the names Irgacure® 184, Irgacure® 1800 and Irgacure® 500 from  
25 Ciba Geigy, Grenocure® MBF from Rahn, and Lucirin® TPO from BASF AG.

In addition to the photoinitiators (D), use may be made of customary sensitizers (D) such as anthracene in effective amounts.

5 Furthermore, the coating material may comprise at least one thermal crosslinking initiator (E). At from 80 to 120°C, these initiators form free radicals which start the crosslinking reaction. Examples of thermally labile free-radical initiators are organic peroxides, organic  
10 azo compounds or C-C-cleaving initiators such as dialkyl peroxides, peroxocarboxylic acids, peroxodicarbonates, peroxide esters, hydroperoxides, ketone peroxides, azo dinitriles, or benzpinacol silyl ethers. Particular preference is given to C-C-cleaving  
15 initiators, since their thermal cleavage does not produce any gaseous decomposition products which might lead to defects in the coating film. Where used, their amounts are generally from 0.01 to 10, preferably from 0.05 to 8, and in particular from 0.1 to 5% by weight,  
20 based in each case on the overall solids content of the coating material of the invention.

Moreover, the coating material may comprise at least one reactive diluent (F) curable thermally and/or with  
25 actinic radiation.

Examples of suitable thermally crosslinkable reactive diluents (F) are branched, cyclic and/or acyclic C<sub>9</sub>-C<sub>16</sub>.

alkanes functionalized with at least two hydroxyl groups, preferably dialkyloctanediols, especially the positionally isomeric diethyloctanediols.

5 Further examples of suitable thermally crosslinkable reactive diluents (F) are oligomeric polyols obtainable from oligomeric intermediates themselves obtained by metathesis reactions of acyclic monoolefins with cyclic monoolefins, by hydroformylation and subsequent  
10 hydrogenation; examples of suitable cyclic monoolefins are cyclobutene, cyclopentene, cyclohexene, cyclooctene, cycloheptene, norbornene or 7-oxanorbornene; examples of suitable acyclic monoolefins are present in hydrocarbon mixtures obtained in petroleum processing  
15 by cracking (C<sub>5</sub> cut); examples of suitable oligomeric polyols for use in accordance with the invention have a hydroxyl number (OHN) of from 200 to 450, a number-average molecular weight Mn of from 400 to 1000, and a mass-average molecular weight Mw of from 600 to 1100.

20

Further examples of suitable thermally crosslinkable reactive diluents (F) are hyperbranched compounds containing a tetrafunctional central group, derived from ditrimethylolpropane, diglycerol, ditrimethylol-  
25 ethane, pentaerythritol, tetrakis(2-hydroxyethyl)-methane, tetrakis(3-hydroxypropyl)methane or 2,2-bis-hydroxymethyl-1,4-butanediol (homopentaerythritol). These reactive diluents may be prepared in accordance

with the customary and known methods of preparing hyperbranched and dendrimeric compounds. Suitable synthesis methods are described, for example, in patents WO 93/17060 or WO 96/12754 or in the book by  
5 G.R. Newkome, C.N. Moorefield and F. Vögtle, "Dendritic Molecules, Concepts, Syntheses, Perspectives", VCH, Weinheim, New York, 1996.

Further examples of suitable reactive diluents (F) are  
10 polycarbonate diols, polyester polyols, poly(meth)-acrylate diols, and hydroxyl-containing polyadducts.

Examples of suitable reactive solvents which may be used as reactive diluents (F) are butyl glycol,  
15 2-methoxypropanol, n-butanol, methoxybutanol, n-propanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl  
20 ether, diethylene glycol monobutyl ether, trimethylolpropane, ethyl 2-hydroxypropionate and 3-methyl-3-methoxybutanol, and also derivatives based on propylene glycol, e.g., isopropoxypropanol.

25 Examples of reactive diluents (F) used that may be crosslinked with actinic radiation are polysiloxane macromonomers, (meth)acrylic acid and other esters thereof, maleic acid and its esters, including

monoesters, vinyl acetate, vinyl ethers, vinylureas, and the like. Examples that may be mentioned include alkylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, 5 vinyl (meth)acrylate, allyl (meth)acrylate, glycerol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolpropane di(meth)acrylate, tripropylene glycol diacrylate, styrene, vinyltoluene, divinylbenzene, pentaerythritol tri(meth)acrylate, 10 pentaerythritol tetra(meth)acrylate, dipropylene glycol di(meth)acrylate, hexanediol di(meth)acrylate, ethoxyethoxyethyl acrylate, N-vinylpyrrolidone, phenoxyethyl acrylate, dimethylaminoethyl acrylate, hydroxyethyl (meth)acrylate, butoxyethyl acrylate, 15 isobornyl (meth)acrylate, dimethylacrylamide, and dicyclopentyl acrylate, and also the long-chain linear diacrylates described in EP-A-0 250 631 and having a molecular weight of from 400 to 4000, preferably from 600 to 2500. The acrylate groups may also, for example, 20 be separated by a polyoxybutylene structure. Further candidates for use are 1,12-dodecyl diacrylate and the reaction product of 2 mol of acrylic acid with one mole of a dimeric fatty alcohol having generally 36 carbon atoms. Mixtures of the abovementioned monomers are also 25 suitable.

Preferred for use as reactive diluents (F) are mono- and/or diacrylates, such as isobornyl acrylate,

hexanediol diacrylate, tripropylene glycol diacrylate,  
Laromer® 8887 from BASF AG, and Actilane® 423 from  
Akcros Chemicals Ltd., GB. Particular preference is  
given to the use of isobornyl acrylate, hexanediol  
5 diacrylate, and tripropylene glycol diacrylate.

Where used, the reactive diluents (F) are employed in  
an amount of preferably from 1 to 70, with particular  
preference from 2 to 65, and in particular from 3 to  
10 50% by weight, based in each case on the overall solids  
content of the coating material of the invention.

The coating material of the invention may comprise  
customary coatings additives (G) in effective amounts.  
15 The nature and amount of the additives (G) are guided  
especially by the intended use of the coating material  
of the invention. Advantageously, the additives (G) are  
not volatile under the processing and application  
conditions of the coating material of the invention.

20

Where the coating material is used as a surfacer FL,  
solid-color topcoat material DL and/or basecoat  
material BL, it mandatorily includes as coatings  
additives (G) at least one filler and/or at least one  
25 color and/or effect pigment (G) in customary and known,  
effective amounts. Preferably, the coating material  
comprises the fillers and/or pigments (G) in amounts of

from 1 up to 95% by weight, with particular preference from 2 to 90% by weight, and in particular from 3 to 85% by weight, based in each case on the overall solids content of the coating material.

5

The pigments (G) may comprise organic or inorganic compounds and may impart color and/or effect. Owing to this large number of suitable pigments (G), therefore, the coating material of the invention ensures a  
10 universal breadth of use of the coating materials and permits the realization of a large number of shades and optical effects.

As effect pigments (G) it is possible to use metal  
15 flake pigments such as commercial aluminum bronzes, aluminum bronzes chromated in accordance with DE-A-36 36 183, and commercial stainless steel bronzes, and also nonmetallic effect pigments, such as perlescent pigments and/or interference pigments, for  
20 example. Examples of suitable inorganic color pigments (G) are titanium dioxide, iron oxides, Sicotrans yellow and carbon black. Examples of suitable organic color pigments (G) are indanthrene blue, Cromophthal red, Irgazine orange and Heliogen green.

25

Moreover the coating material, especially the surfacer FL, may comprise organic and inorganic fillers (G) in customary and known, effective amounts. Examples of

suitable fillers are chalk, calcium sulfate, barium sulfate, silicates such as talc or kaolin, silicas, oxides such as aluminum hydroxide or magnesium hydroxide, or organic fillers such as textile fibers, 5 cellulose fibers, polyethylene fibers, or wood flour. For further details, reference is made to Römpp Lexikon "Lacke und Druckfarben", Georg Thieme Verlag, 1998, pages 250 ff., "Fillers".

10 These additives (G) may also be incorporated into the coating materials by way of pigment pastes, with suitable grinding resins being, in particular, the above-described constituents (A) and also, if appropriate, the above-described constituents (A').

15 These additives (G) are omitted if the coating materials are used, in the context of the process of the invention, as clearcoat materials KL.

20 Examples of suitable additives (G) which may be present both in the clearcoat materials KL and in the surfacers FL, solid-color topcoat materials DL and basecoat materials BL of the invention are

25 - UV absorbers;

- light stabilizers such as HALS compounds, benzotriazoles or oxalanilides;

- free-radical scavengers;
- crosslinking catalysts such as dibutyltin dilaurate or lithium decanoate;
- slip additives;
- 5 - polymerization inhibitors;
- defoamers;
- neutralizing agents such as ammonia or dimethylethanolamine;
- emulsifiers, especially nonionic emulsifiers such as
- 10 alkoxyated alkanols and polyols, phenols and alkylphenols or anionic emulsifiers such as alkali metal salts or ammonium salts of alkanecarboxylic acids, alkanesulfonic acids, and sulfo acids of alkoxyated alkanols and polyols, phenols and
- 15 alkylphenols;
- wetting agents such as siloxanes, fluorine compounds, carboxylic monoesters, phosphoric esters, polyacrylic acids and their copolymers, or polyurethanes;
- adhesion promoters such as tricyclodecanedimethanol;
- 20 - leveling agents;

- film-forming auxiliaries such as cellulose derivatives;
- transparent fillers based on silica, alumina or zirconium oxide; for further details reference is made to Römpp Lexikon "Lacke und Druckfarben", Georg Thieme Verlag, Stuttgart, 1998, pages 250 to 252;
- sag control agents such as ureas, modified ureas and/or silicas, as described for example in the references EP-A-192 304, DE-A-23 59 923, DE-A-18 05 693, WO 94/22968, DE-C-27 51 761, WO 97/12945 or "farbe + lack", 11/1992, pages 829 ff.;
- rheology control additives such as those known from patents WO 94/22968, EP-A-0 276 501, EP-A-0 249 201 or WO 97/12945; crosslinked polymeric microparticles, such as disclosed, for example, in EP-A-0 008 127; inorganic phyllosilicates such as aluminum-magnesium silicates, sodium-magnesium and sodium-magnesium-fluorine-lithium phyllosilicates of the montmorillonite type; silicas such as Aerosils; or synthetic polymers containing ionic and/or associative groups such as polyvinyl alcohol, poly(meth)acrylamide, poly(meth)acrylic acid, polyvinylpyrrolidone, styrene-maleic anhydride or ethylene-maleic anhydride copolymers and their

derivatives, or hydrophobically modified ethoxylated urethanes or polyacrylates;

- flame retardants; and/or

- flatting agents.

5 Further examples of suitable coatings additives (G) of this kind are described in the textbook "Lackadditive" by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998.

The essential factor is that the above-described  
10 coatings additives (G), which may be present both in the surfacers, solid-color topcoats and basecoats and in the clearcoats, do not adversely affect the transparency and clarity of the coating material when it is used as clearcoat KL.

15

The coating material preferably comprises these coatings additives (G), which may be present both in the surfacers, solid-color topcoat materials and basecoat materials and in the clearcoat materials, in  
20 amounts of up to 40, with particular preference up to 30, and in particular up to 20% by weight, based in each case on the overall solids content of the coating material.

Not least, the coating materials of the invention, especially in the case of nonaqueous coating materials, may comprise from 1 to 70, preferably from 2 to 60% by weight (based on the application-ready coating  
5 material), of water-miscible and water-immiscible organic solvents (H), such as aliphatic, aromatic and/or cycloaliphatic hydrocarbons such as toluene or methylcyclohexane or decalin; alkyl esters of acetic acid or propionic acid; alkanols such as ethanol;  
10 ketones such as methyl isobutyl ketone; glycol ethers; glycol ether esters, and/or ethers such as tetrahydrofuran. In the context of the present invention it is also possible to use carbon dioxide as solvent (H).

15

The coating material of the invention may be present in different forms.

Thus, given an appropriate choice of its above-  
20 described constituents (A) and, if appropriate, of at least one of its constituents (A'), (B), (C), (D), (E), (F) and/or (G), it may be present in the form of a liquid coating material which is essentially free from organic solvents and/or water (100% system).

25

However, the coating material may also comprise a solution or dispersion of the above-described constituents in organic solvents (H) and/or water. It

is a further advantage of the coating material of the invention that in this case it is possible to establish solids contents of up to more than 80% by weight, based on the coating material.

5

Moreover, given an appropriate choice of its above-described constituents, the coating material of the invention may be a powder coating material. For this purpose, the constituent (B) may have been  
10 microencapsulated if it is a polyisocyanate. This powder coating material may then, if desired, be dispersed in water, to give a powder slurry coating material.

15 The coating material may be a two-component or multicomponent system in which at least constituent (B) is stored separately from the other constituents and is not added to them until shortly before use. In this case, the coating material of the invention may also be  
20 aqueous, the constituent (B) preferably being present in a component comprising a solvent (H).

Furthermore, the coating material of the invention may be part of a so-called mixer system or modular system,  
25 as described, for example, in patent DE-A-41 10 520, EP-A-0 608 773, EP-A-0 614 951, or EP-A-0 471 972.

Preferably, the coating material of the invention is in the form of an aqueous solution, a dispersion and/or an emulsion, in particular a dispersion, since in this case there is no need to isolate the constituent (A)  
5 for use in accordance with the invention.

The preparation of the coating material from its constituents (A) and also, if appropriate, at least one of its constituents (A'), (B), (C), (D), (E), (F), (G)  
10 and/or (H) has no special features but instead takes place in a customary and known manner by mixing the constituents in appropriate mixing equipment such as stirred vessels, dissolvers or extruders in accordance with the techniques suitable for the preparation of the  
15 respective coating materials.

The coating material of the invention is used to produce the multicoat systems ML of the invention on primed or unprimed substrates.

20

Suitable coating substrates are fundamentally all surfaces which are undamaged by curing of the coatings present thereon using heat and, if appropriate, actinic radiation; examples are metals, plastics, wood,  
25 ceramic, stone, textile, fiber composites, leather, glass, glass fibers, glass wool, rock wool, mineral- and resin-bound building materials, such as plasterboard and cement slabs or roof tiles, and also

assemblies of these materials. Accordingly, the multicoat system of the invention is fundamentally also suitable for applications outside of automotive finishing, in particular for furniture coating and  
5 industrial coating, including coil coating and container coating. In the context of industrial coatings it is suitable for coating virtually all parts and articles for private or industrial use, such as radiators, domestic appliances, small metal parts,  
10 hubcaps or wheel rims.

In the case of electrically conductive substrates it is possible to use primers which are produced in a customary and known manner from electrodeposition  
15 coating materials. For this purpose, both anodic and cathodic electrodeposition coating materials are suitable, but especially cathodic materials.

Using the multicoat system ML of the invention it is  
20 also possible in particular to coat primed or unprimed plastics such as, for example, ABS, AMMA, ASA, CA, CAB, EP, UF, CF, MF, MPF, PF, PAN, PA, PE, HDPE, LDPE, LLDPE, UHMWPE, PET, PMMA, PP, PS, SB, PUR, PVC, RF, SAN, PBT, PPE, POM, PUR-RIM, SMC, BMC, PP-EPDM, and UP  
25 (abbreviated codes in accordance with DIN 7728T1). The plastics to be coated may of course also be polymer blends, modified plastics, or fiber reinforced plastics. It is also possible to employ the plastics

commonly used in vehicle construction, especially motor vehicle construction.

Unfunctionalized and/or nonpolar substrate surfaces may  
5 be subjected prior to coating in a known manner to a pretreatment, such as with a plasma or by flaming, or may be provided with a water-based primer.

The multicoat systems ML of the invention may be  
10 produced in a variety of ways in accordance with the process of the invention.

In a first preferred variant, the process of the invention comprises the following steps:

15

(I) preparing a surfacer film by applying a surfacer to the substrate,

20

(II) curing the surfacer film to give the surfacer coat FL,

25

(III) preparing a solid-color topcoat film by applying a solid-color topcoat material to the surfacer coat FL, and

(IV) curing the solid-color topcoat film to give the solid-color topcoat DL.

In another preferred variant, the process of the invention comprises the following steps:

- 5 (I) preparing a basecoat film by applying a basecoat material to the substrate,
- (II) drying the basecoat film,
- 10 (III) preparing a clearcoat film by applying a clearcoat material to the basecoat film, and
- (IV) jointly curing the basecoat film and the clearcoat film to give the basecoat BL and the clearcoat KL (wet-on-wet technique).

15

A third preferred variant of the process of the invention comprises the steps of:

- 20 (I) preparing a surfacer film by applying a surfacer to the substrate,
- (II) curing the surfacer film to give the surfacer coat FL,
- 25 (III) preparing a basecoat film by applying a basecoat material to the surfacer coat FL,
- (IV) drying the basecoat film,

- (V) preparing a clearcoat film by applying a clearcoat material to the basecoat film, and
- 5 (VI) jointly curing the basecoat film and the clearcoat film to give the basecoat BL and the clearcoat KL (wet-on-wet technique).

Which of the preferred variants is chosen depends on

10 the intended use of the multicoat systems ML of the invention. For instance, the third variant, in particular, is employed with great preference in the context of automotive OEM finishing.

15 Accordingly, the multicoat systems ML of the invention may differ in their structure.

In a first preferred variant of the multicoat system ML of the invention,

20

(1) a surfacer coat FL which absorbs mechanical energy, and

(2) a color and/or effect topcoat DL

25

lie above one another in the stated sequence.

In a second preferred variant of the multicoat system ML of the invention,

(1) a surfacer coat FL which absorbs mechanical  
5 energy,

(2) a color and/or effect basecoat BL, and

(3) a clearcoat KL  
10

lie above one another in the stated sequence.

In a third preferred variant of the multicoat system ML of the invention,  
15

(1) a color and/or effect basecoat BL and

(2) a clearcoat KL

20 lie above one another in the stated sequence. The third preferred variant is employed in particular in the context of coating plastics.  $\mu\text{m}$  [sic]

The application of the coating material in the context  
25 of the process of the invention may take place by any customary application method, such as spraying, knife coating, brushing, flow coating, dipping, or rolling. It is preferred to employ spray application methods,

such as compressed air spraying, airless spraying, high-speed rotation, electrostatic spray application (ESTA), for example, alone or in conjunction with hot spray application such as hot air spraying, for  
5 example. Application may take place at temperatures of max. 70 to 80°C, so that appropriate application viscosities are attained without any change or damage to the coating material and its overspray (which may be intended for reprocessing) during the short period of  
10 thermal stress. For instance, hot spraying may be configured in such a way that the coating material is heated only very briefly in the spray nozzle or shortly before the spray nozzle.

15 The spray booth used for application may, for example, be operated with a circulation system, which may be temperature-controllable, and which is operated with an appropriate absorption medium for the overspray, an example of such medium being the coating material  
20 itself.

Where the coating material includes constituents (C) crosslinkable with actinic radiation, application is made under illumination with visible light with a  
25 wavelength of above 550 nm, or in the absence of light. By this means, material alteration or damage to the coating material and to the overspray is avoided.

The application methods described above may be used to produce all coats FL, DL, BL and KL and also, if desired, further coats.

5 In the process of the invention, the surfacer film, topcoat film, basecoat film and clearcoat film are applied in a wet film thickness such that their curing results in coats FL, DL, BL and KL having the thicknesses which are advantageous and necessary for  
10 their functions. In the case of the surfacer film FL, this thickness is from 10 to 150, preferably from 15 to 120, with particular preference from 20 to 100, and in particular from 25 to 90  $\mu\text{m}$ ; in the case of the topcoat DL it is from 5 to 90, preferably from 10 to 80, with  
15 particular preference from 15 to 60, and in particular from 20 to 50  $\mu\text{m}$ ; in the case of the basecoat BL it is from 5 to 50, preferably from 10 to 40, with particular preference from 12 to 30 and in particular from 15 to 25  $\mu\text{m}$ , and in the case of the clearcoats KL it is from  
20 10 to 100, preferably from 15 to 80, with particular preference from 20 to 70, and in particular from 25 to 60  $\mu\text{m}$ .

In accordance with the invention, the surfacer film,  
25 topcoat film, basecoat film and clearcoat film may be cured thermally, or thermally and with actinic radiation, depending on their material composition. In accordance with the invention it is of advantage to

cure the basecoat film only partly if at all before applying the clearcoat film, and then to cure it together with the clearcoat film (wet-on-wet technique).

5

Curing may take place after a certain rest period. This period may have a duration of from 30 s to 2 h, preferably from 1 min to 1 h, and in particular from 1 min to 30 min. The rest period is used, for example,  
10 for leveling and devolatilization of the coating films or for the evaporation of volatile constituents such as solvents, water or carbon dioxide if the coating material has been applied using supercritical carbon dioxide as solvent (H). The rest period may be  
15 shortened and/or assisted by the application of elevated temperatures up to 80°C, provided this does not entail any damage or alteration to the coating films, such as premature complete crosslinking, for instance.

20

The thermal curing has no special features in terms of its method but instead takes place in accordance with the customary and known methods such as heating in a forced-air oven or irradiation with IR lamps. Thermal  
25 curing may also take place in stages. Advantageously, it is effected at a temperature of from 50 to 100°C, with particular preference from 80 to 100°C, and in particular from 90 to 100°C, for a period of from 1 min

to 2 h, with particular preference from 2 min to 1 h, and in particular from 3 min to 30 min. Where the substrates used have a high capacity to withstand thermal stress, thermal crosslinking may also be  
5 conducted at temperatures above 100°C. In general it is advisable in this case not to exceed temperatures of 180°C, preferably 160°C, and in particular 140°C.

Given an appropriate material composition of the  
10 coating material, the thermal curing may be supplemented by curing with actinic radiation, it being possible to use UV radiation and/or electron beams. If desired, it may be supplemented by or conducted with actinic radiation from other radiation sources. In the  
15 case of electron beams, it is preferred to operate under an inert gas atmosphere. This may be ensured, for example, by supplying carbon dioxide and/or nitrogen directly to the surface of the coating film.

20 In the case of curing with UV radiation, as well, it is possible to operate under inert gas in order to prevent the formation of ozone.

Curing with actinic radiation is carried out using the  
25 customary and known radiation sources and optical auxiliary measures. Examples of suitable radiation sources are high or low pressure mercury vapor lamps, with or without lead doping in order to open up a

radiation window of up to 405 nm, or electron beam sources. The arrangement of these sources is known in principle and may be adapted to the circumstances of the workpiece and the process parameters. In the case  
5 of workpieces of complex shape such as automobile bodies, the regions not accessible to direct radiation (shadow regions) such as cavities, folds and other structural undercuts may be cured using point, small-area or all-round emitters, in conjunction with an  
10 automatic movement means for the irradiation of cavities or edges.

The equipment and conditions for these curing methods are described, for example, in R. Holmes, U.V. and E.B.  
15 Curing Formulations for Printing Inks, Coatings and Paints, SITA Technology, Academic Press, London, United Kingdom, 1984.

Curing may take place in stages, i.e., by multiple  
20 exposure to light or actinic radiation. This may also be done alternately, i.e., by curing in alternation with UV radiation and electron beams.

Where thermal curing and curing with actinic radiation  
25 are employed together (dual cure), these methods may be used simultaneously or in alternation. Where the two curing methods are used in alternation, it is possible, for example, to begin with thermal curing and end with

actinic radiation curing. In other cases it may prove advantageous to begin and to end with actinic radiation curing. The skilled worker is able to determine the curing method particularly appropriate to each  
5 individual case on the basis of his or her general knowledge in the art, possibly with the aid of simple preliminary experiments.

The multicoat systems ML of the invention have an  
10 outstanding profile of properties which is very well balanced in terms of mechanical properties, optical properties, corrosion resistance, and adhesion. Thus the multicoat systems ML of the invention have the intercoat adhesion and high optical quality which the  
15 market requires and no longer give rise to any problems such as inadequate condensation resistance of the surfacer coats, cracking (mud cracking) in the basecoats, or leveling defects or surface structures in the clearcoats.

20

In particular, the multicoat system ML of the invention has an outstanding an outstanding [sic] metallic effect and D.O.I. (distinctiveness of the reflected image) and outstanding surface smoothness. It is stable to  
25 weathering, resistant to chemicals and bird droppings, is scratch resistant, and exhibits very good reflow properties.

A further important advantage is the very good overcoatability of the multicoat system ML of the invention, even without sanding. As a result, it can easily be coated with customary and known, highly  
5 scratch-resistant coating materials based on organically modified ceramic materials.

Not least, however, it proves to be a very particular advantage that by means of the process of the invention  
10 it is possible to produce a multicoat system which is based exclusively on aqueous coating materials.

### **Examples**

#### **15 Preparation Example 1**

##### **The preparation of a dispersion of a copolymer (A)**

A steel reactor as commonly used to prepare  
20 dispersions, equipped with a stirrer, a reflux condenser and 3 feed vessels, was charged with 52.563 parts by weight of DI water and this initial charge was heated to 90°C. The first feed vessel was charged with 10.182 parts by weight of acrylic acid, 18.345 parts by  
25 weight of methyl methacrylate and 1.493 parts by weight of diphenylethylene. The second feed vessel was charged with 9.914 parts by weight of 25 percent strength

ammonia solution. The third feed vessel was charged with 5.25 parts by weight of DI water and 2.253 parts by weight of ammonium peroxodisulfate. With intensive stirring of the initial charge in the steel reactor, the three feed streams were commenced simultaneously. The first and second feed streams were metered in over the course of one hour. The third feed stream was metered in over the course of 1.25 hours. The resultant reaction mixture was held at 90°C for 4 hours and then cooled to below 40°C and filtered through a 100 µm GAF bag. The resultant dispersion had a solids content of from 32 to 34% by weight (1 hour, 130°C) and a free monomer content of less than 0.2% by weight (determined by gas chromatography).

The dispersion (A) was used to prepare a block copolymer (A).

## **Preparation Example 2**

**The preparation of a dispersion of a block copolymer (A)**

A steel reactor as commonly used to prepare dispersions, equipped with a stirrer, a reflux condenser and a feed vessel, was charged with 51.617 parts by weight of DI water and 9.907 parts by weight

of the dispersion from Preparation Example 1 and this initial charge was heated to 90°C with stirring. Thereafter, a mixture of 9.856 parts by weight of n-butyl methacrylate, 7.884 parts by weight of styrene, 12.661 parts by weight of hydroxyethyl methacrylate and 8.885 parts by weight of ethylhexyl methacrylate was metered in from the feed vessel over the course of six hours. The resultant reaction mixture was stirred at 90°C for two hours. Subsequently, the resultant dispersion was cooled to below 40°C and filtered through a 50 µm GAF bag. The dispersion (A) had a solids content of from 41 to 42% by weight (1 hour, 130°C) and a free monomer content of less than 0.2% by weight (determined by gas chromatography).

#### **Example 1**

**The preparation of a multicoat system ML of the invention**

**1.1 The preparation of a surfacer comprising the constituent (A)**

**1.1.1 The preparation of the pigment paste**

For the preparation of the surfacer, first of all a pigment paste is prepared from 3.8 parts by weight of

lamp black, 32.87 parts by weight of barium sulfate (Blanc Fixe® Super-F), 1.73 parts by weight of talc, 1.04 parts by weight of Additol® XW395 (commercial wetting agent) and 60.56 parts by weight of the dispersion (A) from Preparation Example 2. The mixture was predispersed in a dissolver for ten minutes and then ground on a sand mill to a Hegmann fineness < 15  $\mu\text{m}$ . The viscosity of the paste at a shear rate of 100  $\text{s}^{-1}$  and 23°C was 160 mPa.s.

10

#### **1.1.2 The preparation of the surfacer**

The surfacer was prepared by mixing 57.8 parts by weight of the pigment paste from Example 1.1.1 and 30 parts by weight of the dispersion (A) from Preparation Example 2. It had a viscosity of 122 mPa.s at a shear rate of 100  $\text{s}^{-1}$  and 23°C. The surfacer was adjusted with water to a spray viscosity of 55 mPa.s.

### **1.2 The preparation of a metallic basecoat material comprising the constituent (A)**

#### **1.2.1 The preparation of a color paste**

25 For the preparation of the metallic basecoat material, first of all a color paste is prepared from 50 parts by weight of the dispersion (A) from Preparation Example

2, 2 parts by weight of Pluriol® P900 (BASF AG),  
43 parts by weight of Sicopalgelb® L1100 (BASF AG),  
0.4 parts by weight of Agitan® 281 (commercial  
defoamer; Münzing Chemie GmbH). The mixture was  
5 predispersed in a dissolver for ten minutes and then  
ground in a sand mill to a Hegmann fineness < 5 µm. The  
viscosity of the resultant color paste at a shear rate  
of 1 000 s<sup>-1</sup> and 23°C was 424 mPa.s.

10 For mixing with the metallic paste, 62.8 parts by  
weight of the dispersion (A) from Preparation Example 2  
plus 5 parts by weight of water were added to 37.2  
parts by weight of the color paste.

15 **1.2.2 The preparation of a thixotropic agent**

For the preparation of the metallic basecoat material,  
the preparation was carried out additionally of a  
thixotropic agent from 94 parts by weight of DI water,  
20 3.0 parts by weight of Laponite® RD (Solvay Alkali  
GmbH) and Pluriol® P900 (BASF AG).

**1.2.3 The preparation of a polyester dispersion**

25 For the preparation of the metallic basecoat material,  
further, a polyester was prepared in a customary and  
known manner from 23.23 parts by weight of dimer fatty

acid (Pripol® 1009), 10.43 parts by weight of  
1,6-hexanediol, 6.28 parts by weight of hexa-  
hydrophthalic anhydride, 9.9 parts by weight of  
neopentyl glycol and 10.43 parts by weight of  
5 trimellitic anhydride. One part by weight of cyclohexane  
was used as azeotrope former.

The resultant polyester was dispersed in 17.48 parts by  
weight of DI water, 18.9 parts by weight of butyl  
10 glycol and 2.25 parts by weight of dimethylethanol-  
amine.

#### **1.2.4 The preparation of a metallic paste**

15 For the preparation of the metallic basecoat material,  
a metallic paste was prepared from 378.7 parts by  
weight of the thixotropic agent from Example 1.2.2, 74  
parts by weight of a commercial polyester (Maprenal®  
VM 3924), 70 parts by weight of butyl glycol, 334.5  
20 parts by weight of the dispersion (A) from Preparation  
Example 2, 5 parts by weight of a commercial wetting  
agent (BYK® 346), 50.6 parts by weight of a commercial  
aluminum paste (Stapa Hydrolux® 8154), 86 parts by  
weight of the polyester from Example 1.2.3 and 33 parts  
25 by weight of DI water.

The pH of the metallic paste was adjusted to 7.8 using 10% strength dimethylethanolamine solution. The viscosity of the metallic paste was adjusted to 80 mPa.s by further addition of water.

5

#### **1.2.5 The preparation of the metallic basecoat material**

The metallic basecoat material was prepared by mixing the color paste from Example 1.2.1 and the metallic paste from Example 1.2.4 in a weight ratio of 2:10.

#### **1.2.6 The preparation of a clearcoat material comprising the constituent (A)**

15

To produce the multicoat system ML of the invention, a further preparation conducted was that of a clearcoat material from 100 parts by weight of the dispersion (A) from Preparation Example 2, 5 parts by weight of a commercial crosslinking agent based on tris(alkoxycarbonylamino)triazines (Cylink®2000; CYTEC) and 0.4 parts by weight of Agitan® 281. The mixture, which was of low viscosity, was homogenized using an Ultraturrax. Thereafter, the viscosity at a shear rate of 1.00 s<sup>-1</sup> and 23°C was 128 mPa.s.

20

25

**1.2.7 The coating of a substrate with the multicoat system ML of the invention**

To produce the multicoat system ML of the invention,  
5 customary and known steel test panels were used which had been coated with a commercial electrodeposition coating material.

The test panels were coated pneumatically with the  
10 surfacer from Example 1.1. The resultant surfacer film was predried at room temperature for ten minutes and at 80°C for ten minutes. Thereafter it was baked at 100°C for 20 minutes and at 130°C for 20 minutes. This gave a surfacer coat FL with a thickness of 35 µm.

15 The metallic basecoat material from Example 1.2 was applied pneumatically to the surfacer coat FL. The resultant metallic basecoat film was predried at room temperature for ten minutes and at 80°C for ten  
20 minutes.

The clearcoat material from Example 1.2.6 was applied to the predried metallic basecoat film, after which the resultant clearcoat film was flashed off at room  
25 temperature for 15 minutes. Thereafter, the metallic basecoat film and the clearcoat film were baked at 140°C for 30 minutes (wet-on-wet technique). This gave

a metallic basecoat BL with a thickness of 15  $\mu\text{m}$  and a clearcoat KL with a thickness of 35  $\mu\text{m}$ .

The multicoat system ML of the invention produced in this way had an outstanding overall appearance, especially an outstanding metallic effect, an outstanding D.O.I. (distinctiveness of the reflected image), and outstanding surface smoothness. The clearcoat KL was stable to weathering, resistant to chemicals and bird droppings, was scratch resistant, and exhibited very good reflow characteristics.

A further important advantage was the very good overcoatability of the multicoat system ML of the invention, even without sanding. As a result, it was easy to coat the clearcoat KL with customary and known, highly scratch-resistant coatings based on organically modified ceramic materials.